

RATE DETERMINING STEPS STUDY IN CADMIUM SORPTION FROM AQUEOUS SOLUTIONS BY ALMOND PEEL

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ABSTRACT

Batch studies of cadmium sorption by almond peel were carried out to identify the main rate controlling steps in the overall uptake mechanism, using a single external mass transfer diffusion model and intraparticle mass transfer diffusion model. The classical parameters influencing cadmium sorption mechanisms such as: initial cadmium concentration, particle size, agitation speed, temperature, almond peel mass, initial pH solution were investigated. The approach chosen in this study was restricted to an interpretation and subsequent identification of mass transfer coefficients by separating the two mechanisms, based on the adequacy of correspondence models with experimental data of these parameters. The process mechanism was found to be complex, consisting of external mass transfer and intraparticle mass transfer diffusion. Analysis of mechanistic steps involved in the sorption process confirms that the sorption process is particle-diffusion-controlled, with some predominance of some external mass transfer at the initial stages for the different experimental parameters studied.

Keywords: sorption; cadmium; almond peel; external film mass transfer; intraparticle diffusion.

INTRODUCTION

In the field of environmental pollution there are few subjects that, during recent years, have been developed as rapidly as the study of toxic metals. The contamination of water by toxic heavy metals is a world-wide environmental problem. Cadmium, in particular, has received a great deal of attention due to its highly toxic nature and its tendency to accumulate in the tissues of living organisms (Friberg et al. [1]). The main sources of cadmium in streams are effluents from industries such as electroplating, smelting, paints, plastics, battery, zinc mining and refining (Chong & Volesky, [2]). Because of its high toxicity, most countries include cadmium among the "priority pollutants" requiring suitable treatment prior to discharge into the environment (Puranik et al. [3], Butter et al. [4]). At present, a variety of physicochemical processes are employed to treat cadmium-containing effluents. These processes, however, prove

expensive when situations involving high volume and low metal concentration (typically less than 50 mg/L) are encountered (Puranik et al. [3]). Methods such as chemical precipitation and reverse osmosis, as examples, result in incomplete metal removal, have high reagent or energy requirements, and generate toxic sludge which are difficult to dewater and other waste products that require careful disposal (Peters et al. [5], Brierley et al. [6]). Increasing awareness of the environmental impact of metal ions in our water systems has encouraged interest in novel adsorption systems. Recently, considerable research has involved materials of biological origin and many forms of biomass have been shown to be effective metals sorbents. Almond peel waste can be an alternative and favourable sorbent material for pollutants such dyes, heavy metals,...etc. The sorption kinetics of cadmium from aqueous solution by almond peel has been studied (Benaïssa [7]), however, no information are available for its kinetics controlling mechanisms in the literature. Determination of the rate limiting steps in sorption is necessary in order to define the rate parameters for design purposes (Sag & Aktay, [8]). For solid-liquid sorption process, the solute transfer process was usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both.

As a continuation of our work (Benaïssa, [7]), the aim of this study is to investigate the kinetics controlling mechanisms of cadmium sorption by almond peel in batch conditions: external mass transfer and intraparticle diffusion. External and intraparticle diffusion models were separately examined according to the main sorption parameters such as: initial cadmium concentration, agitation speed, initial solution pH, particle size, temperature, and sorbent mass. The approach chosen in this study was restricted to an interpretation and subsequent identification of mass transfer coefficients, based on the adequacy of correspondence models with experimental data of these parameters.

TRANSFER DIFFUSION MODELS

The sorption of solute on solid particles has been extensively studied. It is generally agreed that there are four consecutive steps which describe the overall sorption process of sorption from a solution by a sorbent particle (Furusawa & Smith, [9]). These steps, as adapted to apply to the sorption of metal ions by a sorbent particle, are as follows:

- 1- External mass transfer of the metal ions from the solution bulk to the boundary film;
- 2- Metal ions transport from the boundary film to the surface of the sorbent particle;
- 3- Diffusion of the metal ions within the sorbent particle to the sorption sites: internal diffusion of metal ions;
- 4- Final uptake of metal ions at the sorption sites, via complexation, sorption, or precipitation, which is fast.

The first and the second step are external mass transfer resistance steps, depending on various parameters such as agitation and homogeneity of solution. In this study, the

agitation given to the solution (400 rpm) is considered as sufficient (Benaïssa [7]) to avoid steps 1 and 2 being controlling steps. In a well-agitated batch system, the boundary layer surrounding the particle is much reduced, reducing the external mass transfer coefficient; hence, the third intraparticle diffusion resistance step is more likely to be the rate controlling step (Sag & Aktay, [8]). In the process of establishing the rate limiting step, the fourth step is assumed to be very rapid and is therefore not considered in any kinetic analysis (Findon et al. [10]): sorption is a quasi-instantaneous process, as well as complexation mechanism, precipitation seems to occur with a lower rate (Tsezos & Volesky, [11]). The sorption rate will be controlled by the rate of diffusion (Peniche-Covas et al. [12]). Consequently, the two rate limiting steps investigated are external film mass transfer and intraparticle diffusion, either singly or in combination. Models were established to determine the two coefficients initially based on single resistance mass transport analysis (McKay et al., [13]).

1- External mass transfer resistance model

This model assumes that the surface concentration of solute, C_s , on the sorbent is negligible at $t = 0$, and that intraparticle diffusion is also negligible; it is applied to calculate the initial rate of metal sorption (McKay and Poots, [14]). The initial rate of sorption can be determined using the classic mass transfer equation (1) which describes the evolution of metal ion concentration C_t in solution:

$$dC_t / dt = - \beta_L S (C_t - C_s) \quad (1)$$

Where β_L is the external mass transfer coefficient, C_t the liquid phase solid concentration at a time t , C_s the liquid phase solute concentration at the particle surface and S the specific surface area for mass transfer.

This equation can be simplified, by substituting the following boundary conditions: $C_t \rightarrow C_0$ and $C_s \rightarrow 0$ when $t \rightarrow 0$; C_0 = initial metal ion concentration (McKay et al. [13], McKay & Poots, [14], Weber & Morris, [15]) to:

$$d(C_t / C_0) / dt = - \beta_L S \quad (2)$$

So the external mass transfer rate, $\beta_L S$, is approximated by the initial slope of the C_t / C_0 vs. time graph and can be calculated either by assuming a polynomial relation between C_t / C_0 and time or based on the assumption that the relation-ship was linear for the first initial rapid phase. The first technique was used here.

2- Intraparticle diffusion resistance model

Weber and Morris [15] and McKay et al. [14] demonstrated that in intraparticle diffusion studies, rate processes are usually expressed in terms of square root of time. So q_t or fraction metal sorbed is plotted against $t^{0.5}$ as follow:

$$q_t = kt^{0.5} \quad (3)$$

Where: q_t is the solute concentration in the solid and k the slope of the plot defined as an intraparticle diffusion rate parameter. Initial slope is determined by the derivative (at $t = 0$) of the polynomial linearization of q_t versus $t^{0.5}$. If particle diffusion is rate controlling, the plots q_t versus $t^{0.5}$ are linear and the slope of the plots is defined as an intraparticle diffusion rate parameter, k ($\text{mg metal g}^{-1}\text{sorbent time}^{-0.5}$) (McKay et al., [13] 1986).

In theory, the plot between q and $t^{0.5}$ is given by four regions representing the external mass transfer followed by intraparticle diffusion in macro, meso and micropore (Ho & McKay [16]). From the Fig. 1b (see below, as a typical example), it is observed that there are two linear portions: a first linear portion followed by a second linear portion. The double nature of the curve reflects the two-stage external mass transfer followed by intraparticle diffusion of cadmium onto almond peel particles. The slope of the second linear portion characterizes the rate parameter corresponding to the intraparticle diffusion, whereas the intercept, e (mg/g), is proportional to the boundary layer thickness: the larger intercept the greater is the boundary layer effect (Kumar & Sivanesan [17]). The intraparticle diffusion, k_i ($\text{mg/g min}^{0.5}$), at different experimental conditions, is found from the slope of the corresponding linear region. The calculated k_i values for different experimental conditions are given in Tables 1-6 (see below). In some cases, the linearization of q_t versus $t^{1/2}$ gives a positive and significant ordinate intercept, indicating the influence of external rate control (Slag & Aktay [8]).

As the double nature of the intraparticle diffusion plot, the sorption process is found to be of a complex nature. Thus in order to characterize what the actual rate-controlling step involved in cadmium sorption process is, the sorption data were further analysed by the kinetic expression given by Boyd et al. [18].

$$F = 1 - (6/\pi^2)\exp(-Bt) \quad (4)$$

Where F is the fraction of solute sorbed at different times t and Bt is a mathematical function of F and given by

$$F = q_t/q_\infty \quad (5)$$

Where, q_t and q_∞ represents the amount sorbed (mg/g) at any time t and at infinite time (in the present study? h)

Substituting Eq. (4) into Eq. (5), the kinetic expression becomes:

$$Bt = -0.4967 - \ln(1 - q_t/q_\infty) \quad (6)$$

Thus the value of Bt can be calculated for each value of F using Eq. (6). The calculated Bt values were plotted against time as shown in Figures presented below. The linearity of this plot will provide useful information to distinguish between external transport and intraparticle transport controlled rates of sorption (Kumar et al. [17]). From Fig. 1c (see below, as a typical example), it was observed that the plots

were linear but did not pass through the origin, indicating that, for the all experimental parameters studied here, external mass transport mainly governs the rate-limiting process (Boyd et al. [18]).

The calculated B values can be used to calculate the effective diffusion coefficient, D_i (cm^2/s) using the relation

$$B = \pi^2 D_i / r^2 \quad (7)$$

Where, r represents the radius of the particle calculated by sieve analysis and assuming spherical particles.

MATERIALS AND METHODS

In this work, an agricultural by-product waste: almond peel has been employed as a low-cost sorbent material in the removal of cadmium ions from synthetic aqueous solutions. This waste was collected in summer 2004 from the region of Bensekrane, in Tlemcen-Algeria, in the form of large flakes, cut in small particles of size 1-5 mm and sun/air dried at ambient temperature. It was used as a sorbent material after the following treatment chosen arbitrary: 10 g of almond peel were contacted with 2 L of distilled water in a beaker agitated vigorously (at a speed of 400 rpm) by a magnetic stirrer at ambient temperature of $25 \pm 1^\circ\text{C}$ during 4 hours, then filtered, washed with distilled water for several times until constant pH (4.90-5.75) to remove all the dirt particles, and oven-dried at 80°C for 24 hours after filtration. This material was crushed and sieved into four particles size ranges: 1–1.25; 1.6-2; 2-2.5 and 2.5-3 mm. Except the study of the effect of particle size, only the size 1.6-2 mm was used for further batch sorption experiments.

The experimental systems and procedures have been described elsewhere (Benaïssa [7]).

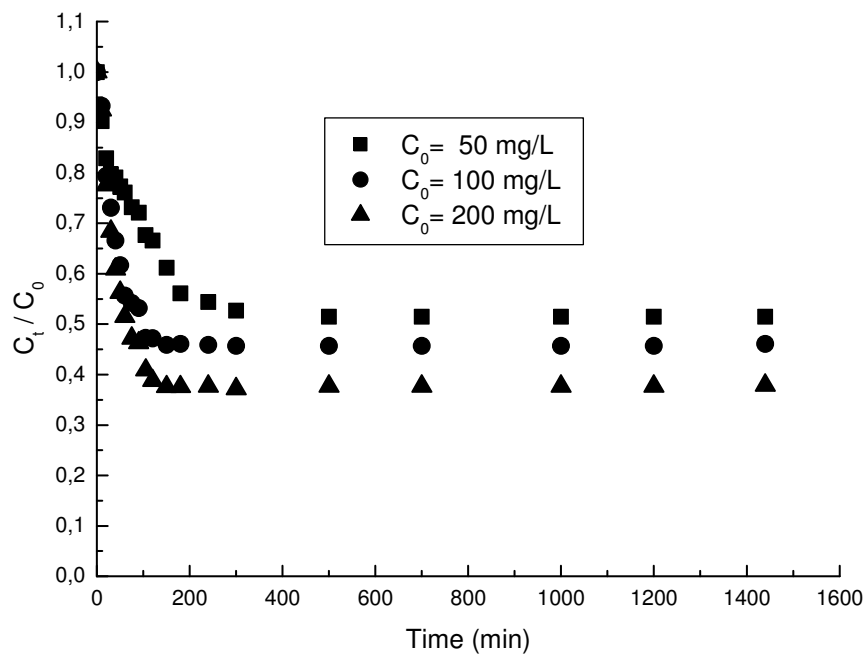
Cadmium solutions of desired concentration were prepared from $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (Windor Laboratories Limited), by dissolving the exact quantities of cadmium salts in distilled water. All chemicals were commercial products used without purification.

RESULTS AND DISCUSSION

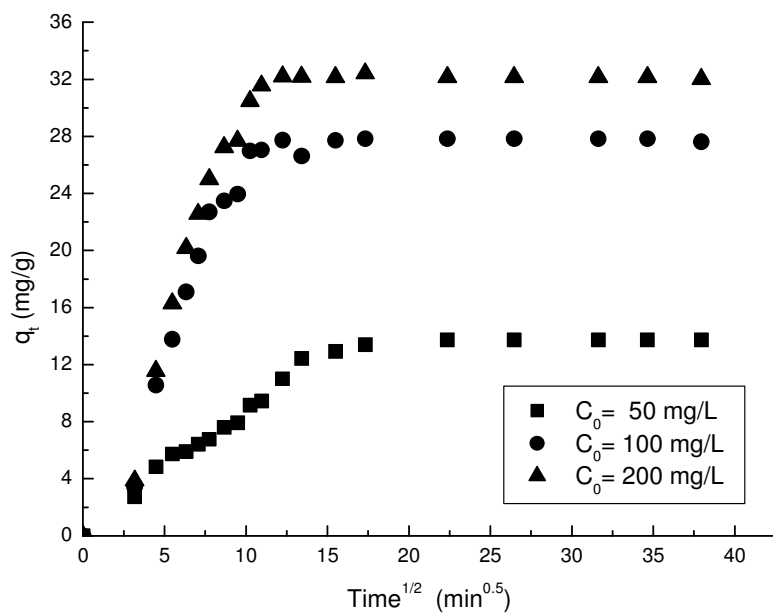
From a mechanistic viewpoint, to interpret the experimental data, it is necessary to identify the steps involved during cadmium sorption, described by external mass transfer (boundary layer diffusion) and intraparticle diffusion.

1- Effect of initial cadmium concentration

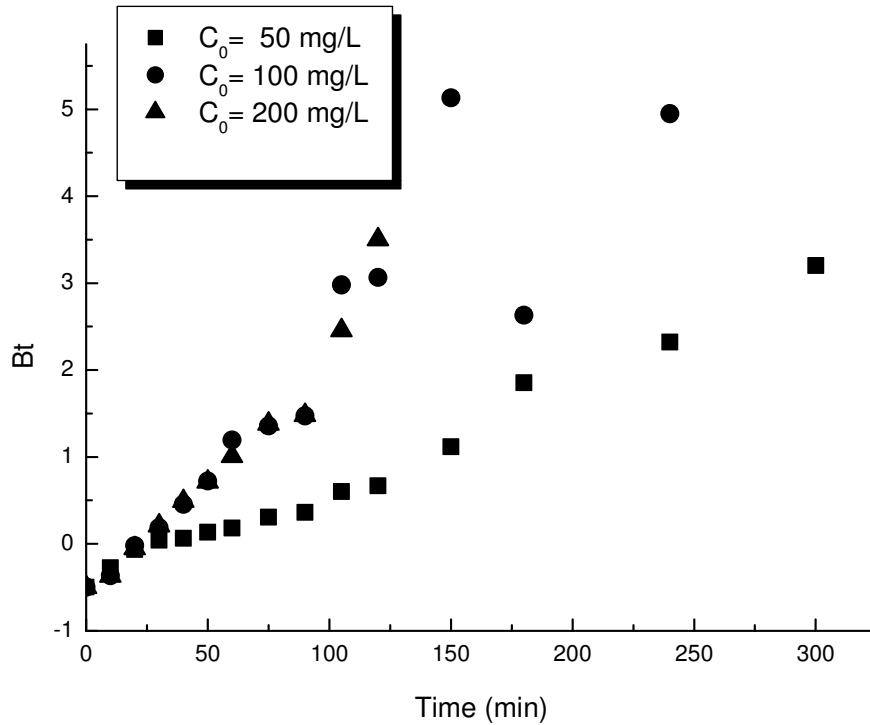
Figures 1a, b and c (as typical examples) show plots of C_t / C_0 versus time, q versus $t^{0.5}$ and Bt versus t for the effect of initial cadmium concentration on cadmium sorption by almond peel. Table 1 summarises the mass transfer coefficients for the different kinds of transfer resistance.



(a)



(b)



(c)

Figure 1: Effect of initial concentration on cadmium sorption kinetics by almond peel: (a) C_t/C_0 versus t , (b) q versus $t^{0.5}$ and (c) Bt versus t .

Table 1: Effect of initial cadmium concentration on diffusion coefficients for cadmium sorption by almond peel. ($m = 2 \text{ g.L}^{-1}$; original solution pH; $d_p = 1.60 - 2.00 \text{ mm}$)
 $N = 400 \text{ rpm}$; $T = 25 \text{ }^\circ\text{C}$)

C_0 (mg/L)	External mass transfer model	Intraparticle diffusion model		Boyd model	
	$\beta_L S \times 10^3 \text{ (min}^{-1}\text{)}$	$k \text{ (mg g}^{-1} \text{ min}^{-0.5}\text{)}$	$e \text{ (mg/g)}$	$B \text{ (min}^{-1}\text{)}$	R^2
50	10.85	0.845	0.41	11.75	0.9784
100	12.37	1.511	10.61	26.65	0.8046
200	12.50	2.054	9.04	30.21	0.9515

From results obtained from Fig. 1a and presented in Table 1, the external film mass transfer coefficient ($\beta_L S$) slightly increases as the initial cadmium concentration increases. This result is consistent with the fact external transport can become the rate-limiting step in systems, which have a dilute concentration of solute (Sag & Aktay, [8]). In Figure 1b showing q versus $t^{0.5}$, two linear regions were observed in the same experiment. McKay et al. [13] explains a non linear plot by a variety of intraparticle

diffusion resistance mechanisms, depending on diffusion through pores of various sizes. The rate of sorption, described as the slope of the plot of the amount of metal sorbed as a function of $t^{0.5}$, increases with initial cadmium concentration.

2- Effect of agitation

Agitation plays an important role in external mass transfer and as result; its influence is restricted to kinetic studies (Saucedo et al., [19]). The constants are determined for the models tested and summarized in Table 2.

Table 2: Effect of agitation speed on diffusion coefficients for cadmium sorption by almond peel. ($C_0 = 100 \text{ mg L}^{-1}$; $m = 2 \text{ g L}^{-1}$; natural solution pH; $T = 25 \text{ }^\circ\text{C}$; $dp = 1.60 - 2.00 \text{ mm}$)

N (rpm)	External mass transfer model	Intraparticle diffusion model		Boyd Model	
	$\beta_{LS} \times 10^3 \text{ (min}^{-1}\text{)}$	$k_i \text{ (mg g}^{-1} \text{ min}^{-0.5}\text{)}$	$e \text{ (mg/g)}$	B (min ⁻¹)	R ²
300	1.67	0.633	/	8.59	0.9633
400	12.37	1.511	10.61	26.65	0.8046
500	6.15	0.374	8.50	16.31	0.9909

Agitation influences the distribution of the solute in the bulk solution but can also act on the formation of the external boundary film. Increasing the agitation speed from 300 to 400 increased the β_{LS} value; this was not unexpected as increased turbulence reduces the film boundary layer surrounding the sorbent particle. Increasing the agitation speed beyond 400 rpm, however, did not raise the β_{LS} value, indicating that external film mass transfer was not the rate-limiting step in a well-agitated vessel. Comparison of intraparticle diffusion coefficients determined for different agitation speeds showed that variation of agitation had little effect on the internal diffusion rate k value. This was not unexpected as agitation only influences the external transport step. The slight effect of agitation implies that external mass transfer is not the sole rate-limiting phase, and confirms that intraparticle diffusion resistance needs to be included in the analysis of overall sorption. These deviations from the models also indicate that single models are not sufficient to describe experimental points accurately (Sag & Aktay, [8]). Experiments with a low agitator speed result in a non-uniform distribution of the sorbent through the solution. External mass transfer and bulk mass transfer therefore have a limited effect on this sorption rate (Guibal et al., [20]). Increasing the degree of agitation increased turbulence that reduces the film boundary layer surrounding the sorbent particle. The results are in agreement with Helfferich [21] who stated that external transport is the rate limiting step in systems which have (a) poor mixing (b) dilute concentrate of sorbate (c) small particle sizes of sorbent and (d) high affinity of sorbate for sorbent.

3- Effect of particle size

Particle size plays an important part in the resistance of the film to diffusion, relating respectively to contact surface (Saucedo et al., [22]). As shown in Table 3, particle size influences the sorption rate. As the particle size is decreased, the external surface of the sorbent particles increased. This decrease in the particle size decreased both the intraparticle diffusion resistance and the external mass transfer resistance. The initial external diffusion rate ($\beta_L S$) was increased by lowering the particle size of the sorbent. Under the same conditions, the intraparticle diffusion rate (k) decreased. Increasing the particle size resulted in a greater time to diffuse to the interior of the particle. The increased particle size will introduce a higher intraparticle resistance and will therefore have a lower internal diffusion coefficient.

Table 3: Effect of particle size on diffusion coefficients for cadmium sorption by almond peel. ($C_0 = 100 \text{ mg L}^{-1}$; $m = 2 \text{ g L}^{-1}$; natural solution pH, $N = 400 \text{ rpm}$, $T = 25 \text{ }^\circ\text{C}$).

dp (mm)	External mass transfer model $\beta_L S \times 10^3 \text{ (min}^{-1}\text{)}$	Intraparticle diffusion model $k \text{ (mg g}^{-1} \text{ min}^{-0.5}\text{)}$ $e \text{ (mg/g)}$		Boyd model $B \cdot 10^3 \text{ (min}^{-1}\text{)}$ R^2	
1-1.25	14.75	1.673	24.26	16.23	0.9923
1.6-2	12.37	1.511	10.61	26.65	0.8046
2-2.5	10.49	0.802	8.19	13.54	0.9740

If the intraparticle diffusion mechanism plays an important part in the control of metal sorption, increasing particle will result in a decrease in sorption rate; the metal ion will therefore have a greater intraparticle distance to diffuse before the sorbent becomes saturated (Guibal et al., [20]). Consequently increasing particle size increases the time needed to reach equilibrium.

4- Effect of temperature

Table 4 represents the diffusion coefficients for models as a function of temperature.

Table 4: Effect of temperature on diffusion coefficients for cadmium sorption by almond peel. ($C_0 = 100 \text{ mg L}^{-1}$; $m = 2 \text{ g L}^{-1}$; natural solution pH, $N = 400 \text{ rpm}$; $dp = 1.60 - 2.00 \text{ mm}$)

T ($^\circ\text{C}$)	External mass transfer model $\beta_L S \times 10^3 \text{ (min}^{-1}\text{)}$	Intraparticle diffusion model $k \text{ (mg g}^{-1} \text{ min}^{-0.5}\text{)}$ $e \text{ (mg/g)}$		Boyd model $B \cdot 10^3 \text{ (min}^{-1}\text{)}$ R^2	
10	9.23	0.525	16.21	9.22	0.9626
25	12.37	1.511	10.61	26.65	0.8046
30	22.31	0.488	22.07	20.60	0.9513
40	24.88	1.345	13.49	21.35	0.9743

The results presented demonstrate that temperature is a parameter which affects the sorption kinetics, within the temperature range studied. In general, an increase in temperature is followed by an increase in the diffusivity of the ion, and consequently by an increase in the sorption rate if diffusion is the rate controlling step. Here in the temperature range studied, an increase in temperature is followed by an increase in the $\beta_L S$ value, and, no clear tendency is observed in the k values.

5- Effect of sorbent mass

The variation in transfer models coefficients at different almond peel doses is given in Table 5.

Table 5: Effect of almond peel mass on diffusion coefficients constants for cadmium sorption. ($C_0 = 100 \text{ mg L}^{-1}$; natural solution pH; $N=400 \text{ rpm}$; $T = 25 \text{ }^\circ\text{C}$; $dp = 1.60 - 2.00 \text{ mm}$)

m (g/300 mL)	External mass transfer model		Intraparticle diffusion model		Boyd model	
	$\beta_L S \times 10^3 \text{ (min}^{-1}\text{)}$		$k \text{ (mg g}^{-1} \text{ min}^{-0.5}\text{)}$	$e \text{ (mg/g)}$	$B.10^3 \text{ (min}^{-1}\text{)}$	R^2
0.3	6.55		1.806	14.26	31.78	0.9872
0.6	12.37		1.511	10.61	26.65	0.8046
1	24.05		0.342	20.74	22.28	0.9839
2	68.66		0.766	8.00	57.81	0.9888

Results show that $\beta_L S$, the external mass transfer coefficient increased with increasing almond peel mass, while the intraparticle mass transfer coefficient k decreased. These observations suggest that the cadmium sorption kinetics by almond peel is largely determined by intraparticle diffusion steps.

6- Effect of initial pH of solution

Solution pH plays an important part in the controlling the rate of sorption. This influence is related to the rearrangement of metal species in the solution and the ionic size of the sorbate influencing the diffusion through the polymer structure (Guibal et al., [20]). Table 6 represents the effect of the initial pH on the values of mass transfer coefficients according to the resistance models tested here. As shown in this Table, as the initial pH of solution increases, the initial rate seems slightly increases, while the particle mass-transfer coefficient k increases. These two phenomena can be assumed to take place combined in different proportions. The results are expected because increasing the initial pH solution results in the formation of cadmium hydroxides ($\text{pH} = 7 - 7.5$) and the diffusion through almond peel is reduced as a result of its larger ionic size.

Table 6: Effect of initial solution pH on diffusion coefficients for cadmium sorption by almond peel. ($C_0 = 100 \text{ mg L}^{-1}$; $m = 2 \text{ g L}^{-1}$; $N = 400 \text{ rpm}$; $T = 25 \text{ }^\circ\text{C}$; $dp = 1.60\text{-}2 \text{ mm}$)

PH ₀	External mass transfer model	Intraparticle diffusion model		Boyd model	
	$\beta_L S \times 10^3 \text{ (min}^{-1}\text{)}$	$k \text{ (mg g}^{-1} \text{min}^{-0.5}\text{)}$	$e \text{ (mg/g)}$	$B \cdot 10^3 \text{ (min}^{-1}\text{)}$	R^2
2	2.29	0.723	2.55	9.14	0.9830
4	2.44	1.390	/	8.36	0.9537
5	10.65	1.070	12.46	17.46	0.9508
7	10.65	1.684	12.47	25.75	0.9751

CONCLUSIONS

Analysis of diffusion mechanisms of cadmium sorption by almond peel was problematic. Diffusion mechanisms were predominant in rate controlling steps. Three models of transfer control were examined: external mass transfer, via a film resistance, the intraparticle diffusion model and Boyd model. These models were not easily applied to evaluate variations in rates and diffusivities. The investigated operating parameters have different effects on mass transfer coefficients. Under our experimental conditions, the analysis of mechanistic steps involved in the cadmium sorption process confirms that the sorption process is particle-diffusion-controlled, with some predominance of some external mass transfer at the initial stages.

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